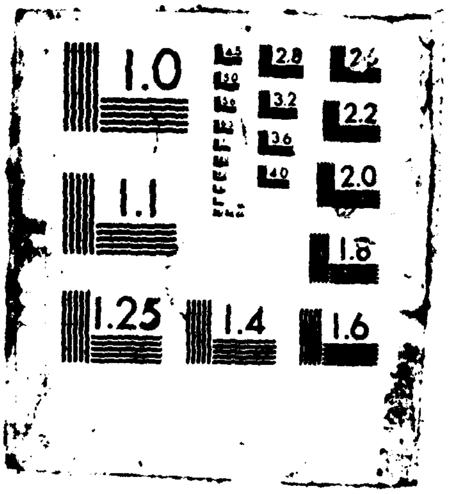
AD-A178 619 CHARACTERIZATION OF DEFECTS CONTROLLING THE DEGRADATION OF HIGH PERFORMAN..(U) STATE UNIV OF NEW YORK AT STONY BROOK DEPT OF MATERIALS SCIEN.. A H KING ET AL. JAN 87 1/1

UNCLASSIFIED ARO-21675.1-MS DAAG29-84-K-0168 F/G 11/3 NL


1.0
2.8
2.5
3.2
2.2
3.6
2.0
4.0
1.1
1.8
1.25
1.4
1.6

ARO 21675.1-MS

(2)

DTIC FILE COPY

AD-A178 619

CHARACTERIZATION OF DEFECTS CONTROLLING THE DEGRADATION OF HIGH PERFORMANCE COATINGS BY JUXTAPOSITION OF TEM AND X-RAY TOPOGRAPHY

FINAL REPORT

DTIC ELECTE APR 2 1987 S D E

A.H. KING and J.C. BILELLO

DTIC COPY INSPECTED 6

JANUARY 1987

Accession For		
NTIS GRA&I	☑	
DTIC TAB	☐	
Unannounced	☐	
Justification		
By		
Distribution/		
Availability Codes		
Dist	Avail and/or Special	
A-1		

U. S. ARMY RESEARCH OFFICE

CONTRACT # DAAG29-84-K0168

Department of Materials Science and Engineering,
State University of New York at Stony Brook,
Stony Brook NY 11794-2275.

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

87 2

MASTER COPY - FOR REPRODUCTION PURPOSES

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

ADA178619

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARO 21675.1-MS	2. GOVT ACCESSION NO. N/A	3. RECIPIENT'S CATALOG NUMBER N/A
4. TITLE (and Subtitle) CHARACTERIZATION OF DEFECTS CONTROLLING THE DEGRADATION OF HIGH PERFORMANCE COATINGS BY JUXTAPOSITION OF TEM AND X-RAY TOPOGRAPHY.		5. TYPE OF REPORT & PERIOD COVERED FINAL. 9/1/84 - 8/31/86 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) A.H. KING AND J.C. BILELLO		8. CONTRACT OR GRANT NUMBER(s) DAAG29-84-K0168
9. PERFORMING ORGANIZATION NAME AND ADDRESS RESEARCH FOUNDATION OF THE STATE UNIVERSITY OF NEW YORK, for and in conjunction with the State University of New York at Stony Brook.		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE Jan. 27, 1987. 13. NUMBER OF PAGES TEN
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

SYNCHROTRON; X-RAY TOPOGRAPHY; TRANSMISSION ELECTRON MICROSCOPY; THIN FILMS; COATINGS; EVAPORATION; SPUTTERING; STRESS; DEFECTS; TUNGSTEN; CHROMIUM; MOLYBDENUM NICKEL; NIOBIUM; SILICON; DIFFRACTION; IMAGING; NON-DESTRUCTIVE EVALUATION

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The techniques of synchrotron x-ray topography and transmission electron microscopy have been combined and applied to the study of defects in evaporated and sputtered thin films on substrates. It has been demonstrated that accurate stress determinations can be made, and defects located, using x-ray topography and that the defects can be analysed in detail using electron microscopy. The combination of the techniques has been shown to be capable of determining defect behaviors that would be inaccessible to either technique in isolation. Keywords;

1. FOREWORD

This report covers the period 9/1/84 to 8/31/86. The project was intended to last for a three year period, but was terminated after only two, in order to allow for a reorganization following the move of Dr. J.C. Bilello from Stony Brook to the California State University at Fullerton. It is intended that the project will continue, with the work at Stony Brook proceeding under a sub-contract from Fullerton, which will hold a contract with the Army Research Office.

The research program was intended to juxtapose two powerful materials characterization techniques that operate in complementary ranges of spatial and distortional resolution. In particular, we planned to use the x-ray topography facilities at the National Synchrotron Light Source (NSLS) for the identification and partial characterization of defects in coatings or substrates, which were then to be further characterized by transmission electron microscopy. Because of delays in commissioning the x-ray ring at NSLS, the x-ray topography facility was not available until May 1985, some nine months after the beginning of this program. This final report, then, covers a research program that has been fully implemented for approximately 15 months, although some preparatory work has been carried out in the period before the topography facilities were available.

2. INTRODUCTION

Thin films on substrates are ubiquitously subjected to harsh environments in engineering systems. The films may be part of the system itself, as in the case of optical coatings or microelectronic integrated circuits, or they may be applied to the surfaces of other materials to provide protection from the environment or to improve the mechanical behavior. In spite of the wide range of applications in which thin films play a critical role, there is still a relatively limited understanding of the ways in which the films may fail, and what can be done to prevent such failures. It is believed that many of the failure modes are associated with crystal defects, either pre-existing in the substrate materials, or somehow induced during the processing steps used in forming the thin film. Even in cases where the film failure mechanism is purely mechanical, theoretical mechanics approaches do not provide very much insight into the failure mechanisms, simply because these approaches can only be used once something is known about the stress-raisers that must be active in causing degradation. For this reason, we have undertaken an experimental program, intended to determine the exact nature of the defects associated with film failure.

In studying the defects that promote the failure of high performance thin films on substrates, we have been obliged to make use of a variety of model systems for experimentation. The most notable way in which this affects the experiments is that we have used single crystal substrates in order to be able to make use of the techniques of synchrotron x-ray topography. Silicon wafers were used for the substrates, because they are readily available, defect free, and of highly reproducible quality. We have used wafers with (100) and (111) surfaces.

It is easy to cleave silicon wafers by striking them at the center with a pointed object. For (100) wafers, this produces four quadrant-shaped pieces from each wafer, and we had intended to use this technique to use each wafer for four different experiments. We found, however, by comparing topographs of whole and quartered wafers, that the cleaving process leaves considerable damage in the wafers, in the form of dislocation tangles. Since we were studying the defects involved in film failure, it was deemed unacceptable to work with such damaged substrates. All of the work reported here was therefore performed using whole, dislocation-free silicon wafers, unless otherwise stated.

Specimens have been prepared by forming thin metallic films on the silicon substrates by thermal evaporation and by ion sputtering in a vacuum. Nickel and chromium films have been formed by evaporation at a variety of thicknesses, on both (100) and (111) substrates. Tungsten, molybdenum and niobium films have been formed by ion sputtering. In every case, the substrate temperature was "ambient" during the course of the processing.

3. SYNCHROTRON TOPOGRAPHY EXPERIMENTS

Synchrotron x-ray topography has been used in order to find defects in the specimens, and also to measure the curvature of the silicon substrates. From the curvature measurements we are able to deduce the stress in the films on the substrates.

White beam synchrotron topographs provide multiple images of the specimens, each with complete coverage. The geometry is essentially similar to that of a Laue camera, but with the film not necessarily placed perpendicular to the incident beam; and in our case each "spot" forms a complete image of the specimen. In this case, of course, the diffracted beams that

form the image come from the single crystal substrate, and not the polycrystalline thin film. The diffracted intensity from the thin film essentially just contributes to the background of the images. When the substrates are perfect and unbent, the white beam images are just uniformly gray, but when there is a defect in the material, the local buckling of the specimen causes strong modulations in the contrast, allowing the defect to be located.

Monochromatic topography has provided information of a rather less graphical nature, but gives a much more quantitative type of information about the substrates. In this type of experiment, diffracted intensity is only produced when the geometry exactly satisfies Braggs' law, so that a curved substrate produces only a single line of diffracted intensity which effectively maps the regions of constant lattice orientation. We have been able to obtain multiple exposures exhibiting such lines, with small changes of specimen orientation between each exposure. The motion of the Bragg contours between the exposures provides an exact measure of the lattice curvature, which allowed us to measure the stresses in our films with a high degree of precision. The stresses, which derive from the formation of the films, are fundamental to the film failure process. It is the stresses that are relieved by the formation of crystal lattice defects, and it is also the stresses that control the ways in which the defects move in order to cause failure of the films.

We have found that the film stresses are largest when the films are thin, and that, in general, they reduce as the films grow thicker. In contrast with this state of affairs, the stress in the substrate should be of the opposite sense, and is constant or increases with increasing film thickness. In line with the conventional wisdom, we have found that the evaporated thin films are usually in a state of tensile stress, and this is consistent with

their being formed at high temperature on a cool substrate, then contracting as they cool to the substrate temperature. The stresses are of the order of 10^{10} dynes/cm^2 and are generally found to be larger, by a factor of two, for (100) than for (111) substrates.

The variation of the film stress with thickness does not appear to be simple, nor even consistent among the materials examined so far. The average film stress for evaporated films decreases inversely with the film thickness; and the average substrate stress increases linearly. This behavior appears to be followed fairly precisely for nickel films over the entire range of thicknesses used. For chromium films, however, there appears to be a saturation effect at a thickness of about 2500Å: the substrate stress ceases to rise beyond this thickness, and remains constant instead. At thicknesses of 5000Å, extensive cracking of the chromium films is observed. At first sight this is surprising, because the film stress reduces as the thickness increases, but for this case the substrate stress increases. It would appear, therefore, that the failure of the coating is associated with a substrate phenomenon of some sort. The cracking of the film usually starts at the specimen edge and branching cracks propagate into the specimen. It is most likely that the cracking of the film is, in large part, responsible for the substrate stress ceasing to rise.

The stress behavior of the sputtered films is very different from that of the evaporated ones. At small thicknesses, both tungsten and niobium exhibit tensile stresses in the film, and compressive in the substrate. For (100) substrates the average film stress decreases rapidly with increasing film thickness, levelling off close to zero at a thickness of about 1000Å. For tungsten, the stress may drop slightly below zero (i.e. become compressive in the film) at a thickness of about 1000Å. The behavior is much more clearly

marked for films on (111) substrates. Both tungsten and niobium form films under tensile stress at small thicknesses, but the sign of the stress reverses at a thickness of about 500Å. For niobium, the average compressive stress in the film levels off at about $3x10^9$dynes/cm^2, but for tungsten it increases to more than $7x10^9$dynes/cm^2.

When tungsten films reach a thickness of 1200Å delamination starts to occur. Again, this is surprising, because the film stress reduces as the thickness increases, but for this case the substrate stress increases. It would appear again, therefore, that the failure of the coating is associated with a substrate phenomenon of some sort. This view is supported by the fact that the delamination occurs in the form of a buckling of the film, with a sinusoidal propagation of the buckle along a well defined direction, and usually staring at the edge of the specimen. The "ordinate" of the sine wave buckle is always aligned parallel to a <110> direction in the silicon substrate. As the thickness of the tungsten films is further increased, the number of wavy buckles increases steadily until the entire film has delaminated.

An interesting aside to the topography studies has been the observation of lines of bright intensity in the background of some of the white beam images. These have not previously been reported and appear to be associated with double diffraction effects that could not be observed without the high intensities and the wavelength range available at the synchrotron light source.

4. TRANSMISSION ELECTRON MICROSCOPY EXPERIMENTS

Transmission electron microscopy studies have been performed principally on the evaporated chromium films. We have performed two different types of study of this system, the first being a general investigation of the film structure, and the second being an investigation of the defects produced in the substrates by the processing steps that we have used.

The specimen preparation for electron microscopy deserves some attention, because it inevitably affects the distribution of stress within the materials. We have prepared our specimens by "back-thinning"; that is to say that we remove the silicon substrate from the uncoated side by chemical means, until the material is electron transparent. This type of specimen allows us to look through a thin layer of the substrate and the coating adhering to the top of it. In some senses, the effect of the thinning process on the internal stresses is the inverse of the effect of building up the coating: as we remove the substrate, the stress in the remaining substrate material should rise while that in the coating should fall. The specimen preparation technique therefore has a tendency to produce more defects in the substrate than would be found in the unthinned material. An additional means of specimen preparation is precision ion milling, using a commercial system known as a PIMS (for Precision Ion Milling System). This system has enabled us to thin specifically chosen areas of a specimen, and also to selectively "drill" holes in the silicon substrates, leaving the coatings unaffected.

A study of the grain size in the coating, as a function of film thickness has revealed that considerable grain growth occurs during the deposition process. At a film thickness of 50Å, the average grain diameter is approximately 40Å for films on both (100) and (111) substrates. The grain size rises linearly with film thickness, at a slightly higher rate for (111) than

for (100) substrates. Eventual grain sizes reach 500Å for films 5000Å thick on (100) substrates. The reasons for this extensive grain growth on essentially "cold" substrates are not yet completely known, but *in-situ* annealing arising from radiant heating from the evaporation source would appear to be likely. We would then expect that the more "structurally relaxed" material would also exhibit the lower stresses, and indeed the material on (111) substrates exhibits the greater grain growth and also the lower stress of the two substrate orientations investigated.

For the thicker films, we have observed extensive cracking, like that observed by x-ray topography, but at a much finer scale. It would appear that the cracks in the film are intergranular.

In some cases, we have observed contrast consistent with slip occurring in the silicon substrates and producing surface steps that are constrained by the overlayer films. The contrast is very similar to that which is referred to as "slip traces" in metals such as aluminum, which have strong, adherent oxide layers which constrain surface steps. A significant difference, however, is that the contrast is observed only for one surface of the silicon, rather than both, as is the case for aluminum, and this is because we only have one surface coated with a surface film. The slip traces thus observed always lie in directions parallel to $\langle 110 \rangle$, just like the buckles in the tungsten films, and parallel to the Burgers vector of the slip dislocations in silicon.

In other cases we have observed the film to be removed in long thin regions parallel to $\langle 110 \rangle_{substrate}$. The substrate in these areas is always severely distorted and contains a high density of dislocations. We have been able to resolve arrays of dislocations in these damaged regions and also occasionally cracks through the substrate. Our preliminary conclusion, then, is

that the failure mode of some of the films involves slip or cracking occurring in the substrates, and this causes incipient buckles or cracks in the films, depending on the sign of the stress. The formation of incipient buckles is particularly important, since buckling of a flat film is theoretically impossible unless an infinite compressive stress exists.

LIST OF PUBLICATIONS AND REPORTS

1. Characterization of thin films by a combination of synchrotron x-ray topography and transmission electron microscopy. W. Ng, M. Namaroff, C.L. Kuo, A.H. King and J.C. Bilello. Presented at MRS Spring Meeting 1986, Palo Alto CA, April 15-18 1986.

LIST OF PARTICIPATING SCIENTIFIC PERSONNEL

1. Mark Namaroff, BE (Engineering Science). Graduate Research Assistant.

2. Waiman Ng, BS (Physics). Graduate Research Assistant.

No degrees were awarded during the funding period.

END

5-87

DTIC